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From O_2/CO_2 to O_2/H_2O combustion: the effect of large steam addition on anthracite ignition, burnout and NO_x formation

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Abstract

Steam-moderated combustion has been proposed to supress flue gas recycling in oxy-fired units, but the influence of replacing CO_2 by H_2O has to be deeply studied. In this paper, oxy-fuel combustion of anthracite with large steam addition has been experimentally characterized, and main results are discussed as concerns the influence upon the ignition temperature, the burnout and the NO_x formation. The tests have been carried out in an electrically-heated entrained flow reactor for a set of O_2/CO_2 and $O_2/H_2O/CO_2$ atmospheres, with steam addition up to 40 % vol. The results show that ignition temperature diminishes when steam is added in low rates (maximum decrease of 16 ºC), but the trend is reversed for the higher steam concentrations (maximum increase of 18 ºC). The effect of steam addition on coal burnout rates is more significant for the 21 % vol. O_2 atmosphere, with a decrease of 2.2–5.3 percentage points, and almost negligible for the 35 % vol. O_2. An outstanding reduction of NO specific emissions is detected when adding H_2O, with decrements ranging 28–45 % compared to the dry conditions. The transition from O_2/CO_2 combustion to O_2/H_2O combustion barely affects the anthracite conversion but significantly diminishes NO_x formation rates.

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Keywords

Oxy-combustion; Steam moderation; Anthracite; Ignition; Burnout; NO_x emissions

Nomenclature

ASU	Air separation unit
CCUS	Carbon capture, use and storage
CPU	Compression and processing unit
DTF	Drop tube furnace
EFR	Entrained flow reactor
T_{bo}	Burnout temperature (ºC)
T_{ig}	Ignition temperature (ºC)
T_p	Pre-ignition temperature (ºC)
XRD	X-ray diffraction
[X]	Molar concentration of species X (–)
α	Ash weight fraction, dry basis (–)
β	Burnout degree (%)
λ	Oxygen excess over stoichiometry (–)

1. Introduction

According to a recent IEA report [1], global energy demand will increase by more than a quarter to 2040. Despite there is a great scope for renewable energies to increase, coal will still playing a major role in bringing affordable, reliable electricity to millions of people in the near and medium term [2]. Coal world consumption increased by 0.7 % during 2018 after two years of decline, while CO_2 emissions level has recently reached its highest value with 33.4 Gton [3].

Consequently, the deployment and application of all clean energy technologies, including CO_2 capture in coal-fired power plants, is necessary and urgent.

Carbon Capture, Use and Storage (CCUS) technologies are internationally recognised as indispensable ways to meet climate targets. Carbon capture systems in fossil fuel-fired plants have been worldwide proved with 21 large-scale integrated projects in operation or under construction [2]. Among them, oxy-fuel combustion consists on firing fuels in enriched-O_2 environments, free of N_2, producing flue gases mostly composed by CO_2 and suitable for compression and storage. Recycling of about 60 % of the total flue gases [4] is needed to moderate the temperature in the furnaces and get flame stability. Several issues have been researched during the last years in relation to fuel conversion, fluid dynamics, heat transfer and pollutants formation in oxy-fired systems, aiming at determining the optimal O_2/CO_2 composition in comparison to the well-known air-fired performance [5–6].

Main challenges for the development of oxy-fuel combustion plants are related to the reduction of the large energy penalties caused by ASU and CPU stages (air separation unit and compression and processing unit, respectively), with a target of 7-9 % [7]. Besides energy integration and optimization, other solutions can also contribute to increase the efficiency and operating manageability of these plants. One possibility is the full avoidance of recycling flue gases, or alternatively the replacement of CO_2 by H_2O to dilute the oxygen (the so-called oxy-steam combustion). This was initially suggested by Salvador [8], and represents a chance beyond the concept of wet recycling in which a rate of the flue gases returns to the boiler without any previous condensation. Several authors have reported the advantages of the oxy-steam combustion by simulating full-scale concepts [9–12]. These advantages can be summarized in the following items: 1) simpler plant layout, 2) reduction of boilers size, 3) decrease of gas cleaning requirements, 4) decoupling the furnace operation and the flue gas recycling, 4) reduction of the ancillaries consumption, 5) reduction of the air in-leakages.

There are already some published results concerning lab-scale research of coal oxy-combustion with a different extent of steam addition rates. They are mostly focused on the ignition behaviour of a single particle, or a cloud of few particles, in drop tube furnaces (DTF) equipped with cameras: Kops et al. [13] used a high-speed camera to record and characterize the ignition process of three solid fuels

(two coals and one biomass) under steam addition up to 10 % vol.; Lei Cai et al. [14] evaluated the influence of steam addition, up to 30 % vol., during oxy-combustion of bituminous coals using a high-speed camera; Chun Zou et al. [15] developed ignition tests of a bituminous coal under 79/21 % H_2O/O_2 atmosphere in a DTF with a high-speed camera and a two-colour pyrometer; Hao Zhou et al. [16] investigated ignition, flame temperature and burnout of an anthracite coal and a biomass in 79/21 % H_2O/O_2 atmosphere by using a CCD camera; Kai Lei et al. [17, 18] conducted a similar study for blends of a bituminous coal and different biomasses, under steam fractions up to 79 % vol., by using a high speed camera. A common outcome from these papers is that steam addition reduces ignition temperature and delay times, but with different extents depending on the fuel type and the steam concentration. Only the work by Riaza et al. [19] addressed the question for larger fuel rates, in an entrained flow reactor (EFR), for steam concentrations ranging from 5% vol. to 20 % vol.

The number of experimental works addressing the effect of steam addition on NO_x emissions during oxy-fuel combustion is very scarce, and with limited steam rates. Morón et al. [20] characterized NO_x emissions under a 10 % steam atmosphere by oxy-firing coal and biomass in an EFR. Shujun Zhu [21] studied the NO emission in a down-fired combustion chamber in which the pulverized coal was burned under a maximum steam content of 17 % vol. Alvarez et al. [22] determined the NO emissions of a semi-anthracite and a high-volatile bituminous coal under oxy-fuel combustion conditions in an EFR replacing CO_2 by 5, 10 and 20 % of steam. Zhijun Sun et al. [23] developed experiments for an anthracite and a bituminous coal with oxy-atmospheres from 10 % to 40 % H_2O in a DTF. The results from these works do not lead to a common conclusion: in most cases a small addition of steam (5-10 % vol.) yields NO reduction [20, 22, 23], but different trends are reported for concentrations over 10 % vol. H_2O.

According to this review, limited oxy-combustion studies with large steam concentrations have been previously reported, aside from those focused on the ignition of single/few particles. In the present work, a simultaneous study of ignition, fuel conversion and pollutants formation is presented and discussed, covering a lack in the already published experiences. This is the first work addressing a comprehensive experimental characterization of oxy-coal combustion with the addition of high steam percentages replacing CO_2 (up to 40 % vol. H_2O) in an entrained flow reactor. Original contributions are included towards the concept

of oxy-steam combustion: an extensive set of ignition temperatures, burnout degrees and fuel-NO conversion rates are provided for nine $O_2/CO_2/H_2O$ atmospheres, and compared to O_2/N_2 and O_2/CO_2 conditions.

2. Facility and experimental tests

2.1 Description of the facility

Figure 1 displays a diagram of the lab-scale plant. It mainly consists of a fuel feeding system, a gases-water mixing and supply system, an entrained flow reactor, a collecting probe and a condenser. The reactor is made of a Kanthal alloy, electrically heated by four independent furnaces and able to operate up to 1150ºC. The internal diameter is 0.038 m and the height can be varied, by a bottom-movable sampling probe, in the range 0.8 – 1.6 m.

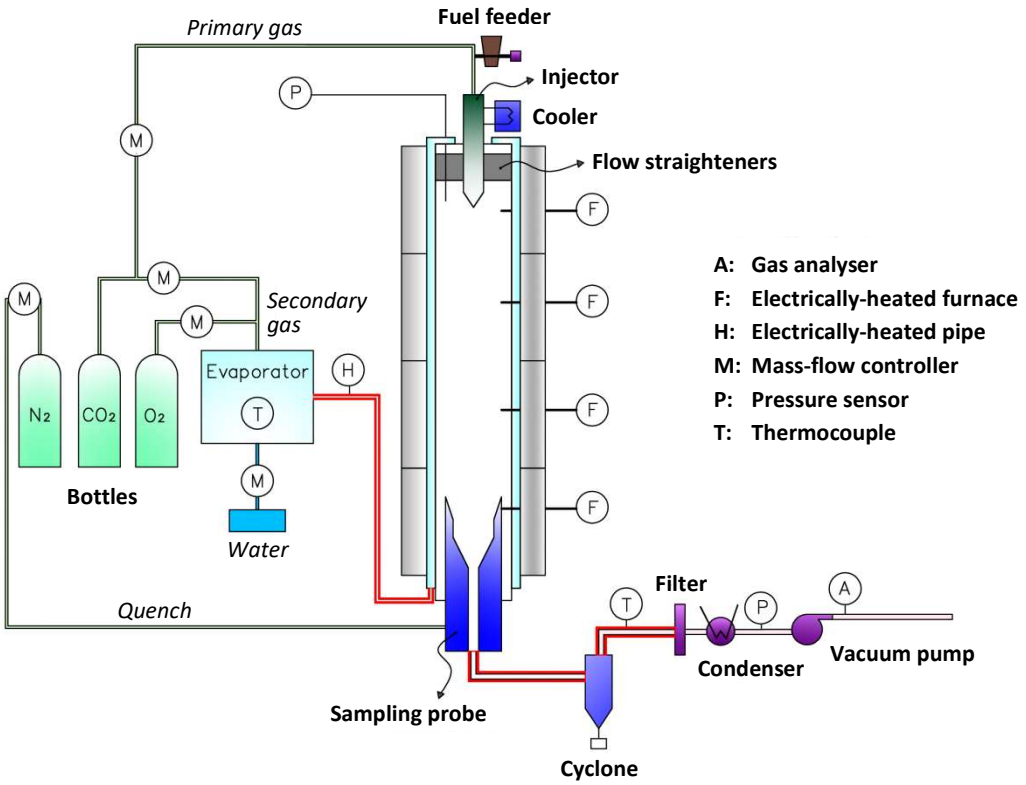

Figure 1.- Diagram of the lab-scale entrained flow reactor.

The fuel is supplied by a mechanical screw to the primary gas flow, entering the reactor through a water-cooled injector. The secondary gas flow is preheated by

risers inside the electrical heaters and then directed downwards the reactor through a flow straightener. Gases supply from bottles is provided by several mass flow controllers and, if required, one Coriolis flow meter controls the water flowrate. The uncertainties of mass flow measurements are 0.5 % for the gases and 0.2 % for the water. An external evaporator/mixer is used to get the prescribed composition for the firing atmosphere.

Nitrogen is introduced at the bottom of the reaction section, through round holes in the upper part of the collecting probe, to quench the combustion products. After the reactor, fly solid residues are retained by a cyclone and a filter. When large concentrations of steam are supplied, a condenser is used to retain most of the flue gases moisture. A continuous emission monitoring system is connected on-line to the process, providing the flue gas composition at the cold-end section: NDIR Siemens Ultramat for SO_2 (0–3000 ppm vol.), NO (0–1000 ppm vol.), CO_2 (0–100 % vol.) and CO (0–5000 ppm vol.), and paramagnetic Siemens Oxymat for O_2 (0–25 % vol.). The uncertainties of these measurements are 1% full-scale.

The phase composition of the crystalline species of the solid residues gathered after each test was investigated applying XRD, using a Siemens Bruker D8 Advance Series 2 diffractometer set to select Cu Kα radiation (the diffraction angle scanned was 20–60° 2 θ using a step size of 0.05° 2 θ). Unburned content in solid residues were obtained in a Hobersal HD-230 muffle furnace.

2.2 Fuel

The coal fired during the experimental campaign was anthracite from northern Spain. This is a difficult fuel, with a very low content of volatiles and a high content of ash. Information about proximate and ultimate analysis is shown in Table 1, along with the low heating value and the ashes composition. The coal was milled and sieved in the range 75–150 μm to proceed with the ignition and combustion tests.

Large reserves of anthracite are proved in USA and Asia-Pacific region. In the latter, around two thirds of power generation still relies on coal combustion and anthracite plays a role [3]. Anthracite is a difficult coal to fire, but oxy-fuel combustion widens its possibilities due to the O_2 enrichment in comparison to conventional combustion.

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Coal analysis		
Proximate analysis (% wt., as fired)		
	Moisture	1.8
	Volatile matter	5.4
	Fixed carbon	66.4
	Ash	26.4
Ultimate analysis (% wt., daf)		
	Carbon	92.9
	Hydrogen	2.1
	Nitrogen	1.2
	Sulphur	1.2
Heating value		
LHV (kJ/kg, as fired)		23 100
Ashes		
Ashes composition (% wt.)		
	Al_2O_3	24.78
	CaO	2.83
	Fe_2O_3	8.26
	K_2O	3.22
	MgO	1.56
	Na_2O	0.70
	SiO_2	47.20
	TiO_2	0.99

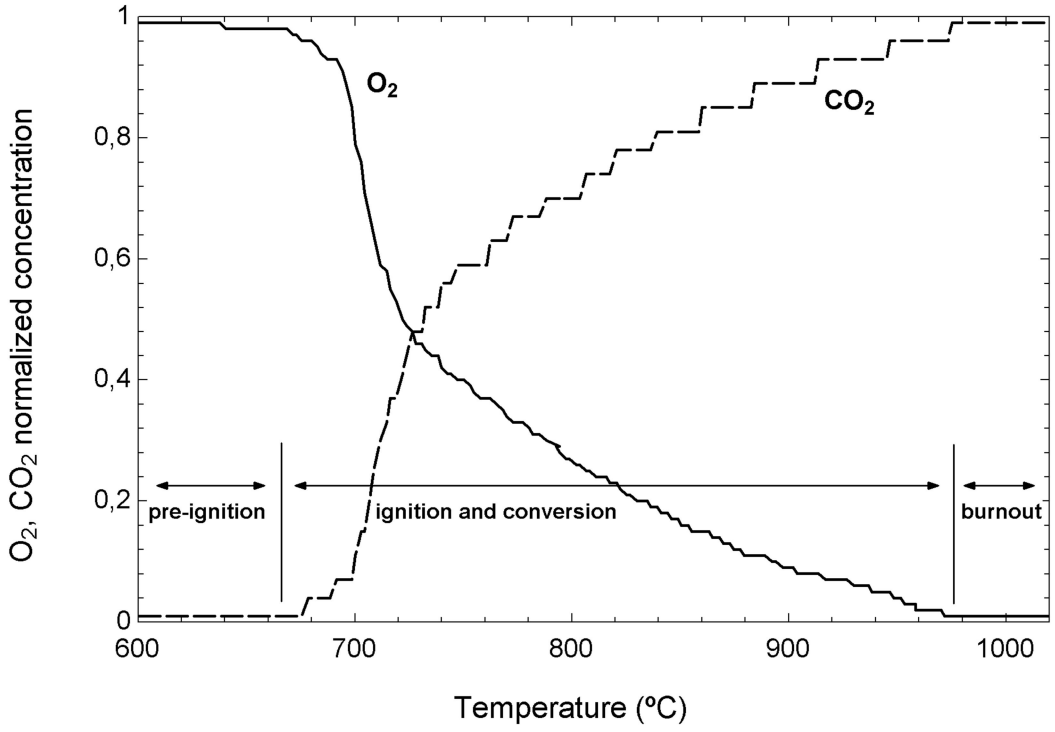
Table 1.- Anthracite analysis, heating value and ashes composition.

2.3 Experimental conditions for ignition tests

Ignition temperatures were experimentally determined by 9 specific trials in the entrained flow reactor. The tests comprised air, a pair of O_2/CO_2 (21 % and 35 % O_2) and six $O_2/CO_2/H_2O$ atmospheres, with steam ranging from 10 % to 40 % vol. (for 21 % and 35 % O_2). The unit was heated from ambient temperature to 1000 ºC with a rate of 15 ºC/min. The coal was fed from a temperature of 400 ºC.

An indirect method based on the evolution of the O_2 and CO_2 concentrations in flue gases was used to determine the ignition temperature of the anthracite. Similar approaches have been reported previously by other authors for the same type of reactor [24, 25] but for lower steam concentrations. Figure 2 illustrates the evolution of O_2 and CO_2 molar concentrations as a function of the gas temperature

187 in the reactor during an ignition tests (units have been normalized in the range
188 0–1, in order to show a generic case). Three different zones can be distinguished:
189 1) pre-ignition, where the first derivative of the concentrations can be neglected,
190 2) ignition and conversion of the particles, where the concentrations quickly evolve
191 while the gas temperature increases, and 3) steady evolution when burnout is
192 reached, where again the concentrations remain constant.



193

194 **Figure 2**.- Normalized O_2 and CO_2 molar concentration in flue gases during the ignition test.

195

196 Based on the approaches reported in references [24, 25], we adopt the following
197 calculation to determine the ignition temperature:

198

199 $$\left|\frac{[X(T_{ig})]-[X(T_p)]}{[X(T_{bo})]-[X(T_p)]}\right| = 0{,}1 \quad (1)$$

200

201 where *[X(T)]* stands for the O_2 or CO_2 molar concentration for each temperature.
202 The ignition temperature T_{ig} was obtained by averaging the results obtained from
203 O_2 and CO_2 measurements.

204

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2.4 Experimental conditions for combustion tests

Four different atmospheres were selected to conduct the combustion experiments: air, 21/79 % O_2/CO_2, 30/70 % O_2/CO_2 and 35/65 % O_2/CO_2 (from here onwards, all concentrations are given in volume basis unless other indicated). The initial reactor temperature was kept at 1000 ºC for all the combustion tests, while reactor height was set to 1.5 m. To seek the effect of steam moderation, water was added to the oxy-firing atmosphere replacing CO_2: 10 %, 25 % and 40 % for a fixed value of oxygen excess (λ = 1.25). Flow rates were then selected to result in a mean residence time of 3 s. The values are summarised in Table 2 for the 13 combustion tests. The experiments are defined to keep constant the residence time of the coal inside the reactor. Since the tests are carried out under entrained flow conditions, to keep the same residence time means a constant gas volumetric flow rate. Due to the different atmospheres tested, coal mass flow rate is not the same and neither the gas mass flow rate.

Test #	**Atmosphere** (% vol.)	**Coal flow rate** (g/min)	**O_2 flow rate** (g/min)	**CO_2 flow rate** (g/min)	**Water flow rate** (g/min)
1	21/79 O_2/N_2	0.60	1.42	4.69 (N_2)	–
2	21/79 O_2/CO_2	0.60	1.42	7.37	–
3	21/69/10 O_2/CO_2H_2O	0.60	1.42	6.44	0.38
4	21/54/25 O_2/CO_2H_2O	0.60	1.42	5.04	0.95
5	21/39/40 $O_2/CO_2/H_2O$	0.60	1.42	3.64	1.53
6	30/70 O_2/CO_2	0.86	2.02	6.49	–
7	30/60/10 $O_2/CO_2/H_2O$	0.86	2.02	5.56	0.38
8	30/45/25 $O_2/CO_2/H_2O$	0.86	2.02	4.17	0.95
9	30/30/40 $O_2/CO_2/H_2O$	0.86	2.02	2.78	1.52
10	35/65 O_2/CO_2	0.99	2.35	6.00	–
11	35/55/10 $O_2/CO_2/H_2O$	0.99	2.35	5.08	0.38
12	35/40/25 $O_2/CO_2/H_2O$	0.99	2.35	3.69	0.94
13	35/55/40 $O_2/CO_2/H_2O$	0.99	2.35	2.31	1.51

Table 2.- Mass flow rates during the combustion tests (λ = 1,25).

In order to assess the effect of steam addition on NO_x emissions in comparison to the influence of oxygen excess, 6 additional tests were carried out for the three O_2/CO_2 dry atmospheres with λ = 1.35 and λ = 1.45. Flow rates were again selected to get a residence time of 3 s inside the reactor, for the mean particle size.

Coal burnout degree β was calculated after each combustion test, according to the following definition:

$$\beta = \frac{\alpha_f - \alpha_i}{\alpha_f\,(1-\alpha_i)} \quad (2)$$

where α_f is the ash weight fraction (dry basis) in the solid residues recovered in the cyclone and α_i is the ash weight fraction (dry basis) in the fired coal. Ash weight fractions in residues, all they collected under steady-state conditions, were determined according to the standard UNE-32-004-84; accuracy of the weighing device was ±0.0001 g. Burnout degree β accounts for the solid-to-gas conversion rate, but not for the full conversion of the gas-phase compounds to final products. To obtain a more complete picture, CO emissions in flue gases are also provided in the section 3.2.

3. Results and discussion

3.1 Ignition temperature

The results for the ignition temperatures are displayed in Figure 3. The accuracy of the temperature measurements is ±2 ºC. The first effect that can be observed in the Figure 3 is an increase of 15 ºC in the ignition temperature when N_2 in air is replaced by CO_2. This trend is consistent with previous works [19, 26, 27] and is explained by the higher value of the molar specific heat of CO_2 in comparison to that of N_2. This leads to a reduction of the temperature in the surroundings of the particle during oxy-combustion in comparison to air combustion, for the same oxygen concentration (21 %), and then a reduction of the oxidation rates of volatiles and char with the consequent delay of the ignition. Nevertheless, the effect is moderate in our case, which is explained by the very low amount of volatiles in the tested coal.

As concerns the effect of steam addition, when 10% H_2O is added as CO_2 substitution there is an advancement of 16 ºC in the ignition temperature for the 21 % O_2 atmosphere. This is the contrary effect to the previously explained, since the molar specific heat of H_2O is lower and then an increase of burning rates happens in the surroundings of the particles, due to the higher temperatures. The advancement is much lower (4 ºC) in the 35% O_2 case.

Nevertheless, the trend shifts when 25% H_2O is added, what is a new insight. On the one hand, the thermal diffusivity of steam is higher than the N_2 and CO_2 ones, which partially counterbalances the previous advancement. On the other hand, steam enhances char gasification and CO local concentration depletes the O_2 in the proximity of the particle. Besides, this endothermic gasification also contributes to a decrease of the particle temperature. When steam is further increased up to 40%, the behaviour is different depending on the oxygen content. There is an additional delay (6 ºC) for the 21% O_2 case, but the ignition temperature remains almost unaltered for the 35% O_2 case (the difference falls within the measurement accuracy range). The higher O_2 content and diffusivity explain this observation. These effects were not detected by thermogravimetric tests for the same coal and atmospheres [28] due to the very high mass ratio oxidant-to-fuel, not as realistic as the used in the EFR unit (λ = 1.25).

Concluding, and according to our results, the "U-shape" trend observed in the Figure 3 eventually leads to a very small variation of the temperature ignition for the 21/40 % O_2/H_2O and 35/40 % O_2/H_2O atmospheres in comparison to the dry ones: +2 ºC and +4ºC respectively.

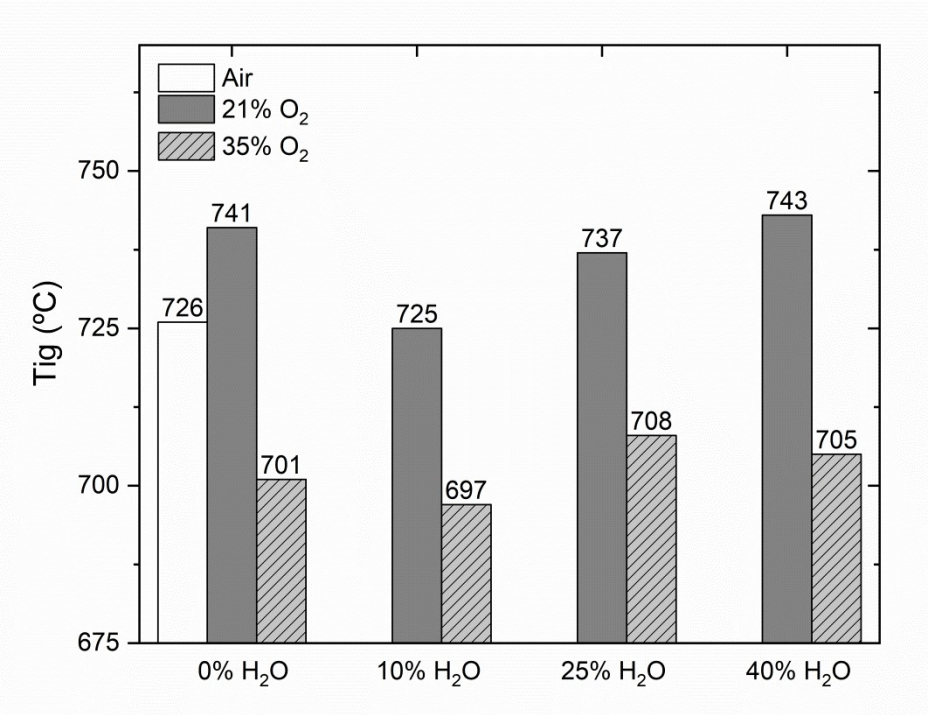

Figure 3.- Ignition temperatures under different atmospheres (steam is added as CO_2 replacement).

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3.2 Burnout

Figure 4 shows the influence of the atmosphere composition (for different $O_2/CO_2/H_2O$ proportions) over the coal burnout. The effect of including steam in the atmosphere for different O_2 percentages (λ = 1.25) is illustrated. When steam was added to the oxidizer stream in a proportion of 10 % and 25 %, the burnout degree decreased significantly for the atmosphere containing 21% O_2: 2.9 and 5.3 percentage points respectively. Burnout was barely affected (0.6–1.5 percentage points) in the case of the environments containing 30 % O_2 and 35 % O_2. The results obtained for the lower H_2O percentages agree with the conclusions obtained by Riaza et al. [19]. These authors reported that the addition of steam in 5 %, 10 % and 20 %, under oxy-fuel combustion atmospheres with 30 % and 35 %O_2, did not significantly affect the coal burnout. The decrease in burnout observed in Figure 4 when adding steam to the 21% O_2 dry atmosphere (tests #3 and #4) is explained by the reduction of the char specific surface for H_2O in comparison to CO_2 [29], what is significant for a coal with so low volatile content.

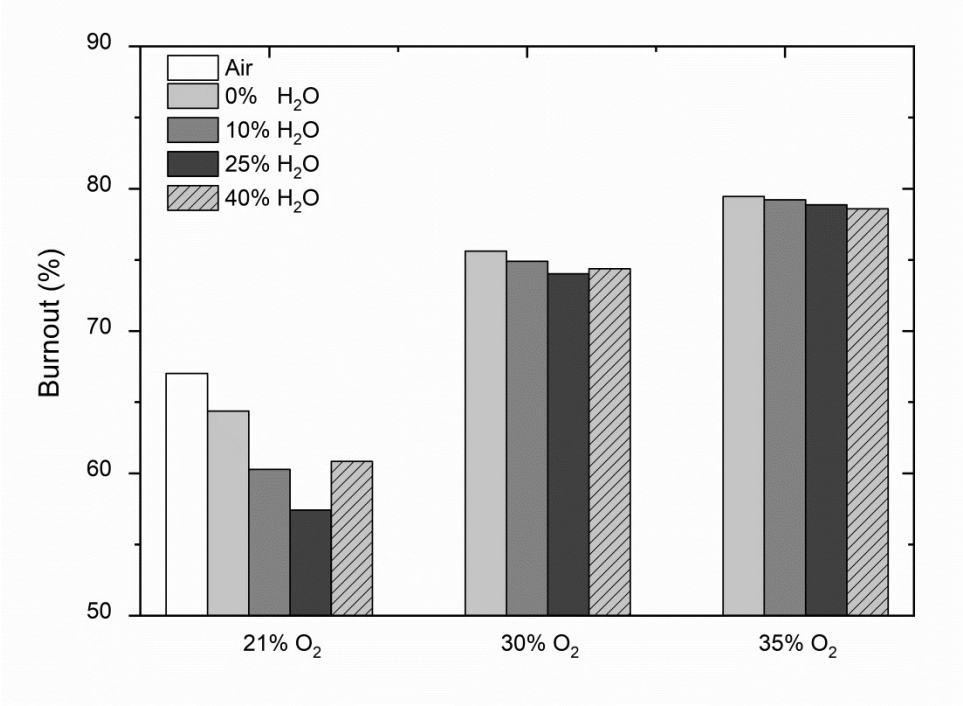
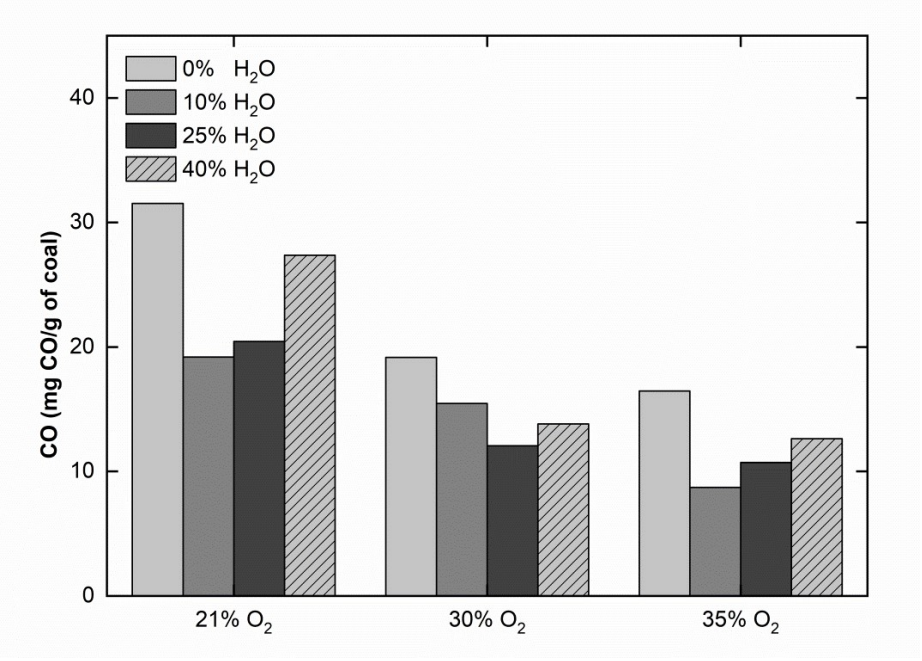


Figure 4.- Comparison of burnout obtained under different H_2O and O_2 conditions.

When the highest steam proportion was added (40 %), the burnout obtained at 21% O_2 increased 3.1 percentage points (in comparison to the 25 % H_2O case). This is explained by the reverse influence caused by the increase of both the

299 temperature (due to the specific heat of steam) and the O_2 diffusivity. Again,
300 burnout remained almost invariable when adding 40 % H_2O for the higher O_2
301 contents studied (30 % and 35 %), pointing out the prevailing effect of the
302 O_2 concentration over the H_2O one. This attenuation of the burnout increase when
303 $\%O_2$ rises is explained by the competition between char gasification (by CO_2 and/or
304 H_2O) and char oxidation (by O_2) in the oxy-fired conditions. Baojun Yi et al. [30]
305 studied the impact of O_2 and H_2O on the combustion characteristics of pulverized
306 coal in $O_2/CO_2/H_2O$ atmospheres in a drop tube furnace. These authors deduced
307 that the extent of H_2O gasification is attenuated for O_2 concentrations higher
308 than 30 %.

309 Burnout degree can be also influenced by the extent of char gasification
310 reactions. Figure 5 displays CO specific emissions (per fuel mass unit) at reactor
311 outlet for each test. As can be seen, a clear decrease of CO was obtained when
312 adding 10 % H_2O in comparison to the dry atmosphere, for all the O_2 percentages.
313 The larger mass diffusivity of oxygen in H_2O (in comparison to CO_2) increases CO
314 oxidation to CO_2 in the gas phase.



315

316 **Figure 5.-** Comparison of CO specific emissions obtained under different H_2O and O_2 conditions.
317

318 When the steam concentration is increased to 40 % vol., CO concentration in flue
319 gases increases with a different extent depending on $\%O_2$. Release of carbon
320 monoxide by char gasification is enhanced due to the high H_2O concentration, but

CO presence in flue gases at reactor outlet is attenuated for the richer atmospheres due to the larger O_2 availability. Anyway, CO levels are always lower under $O_2/CO_2/H_2O$ atmospheres in comparison to O_2/CO_2 for the same O_2 concentration: the observed decrease ranges from 13 % to 23 % when comparing the dry cases to the 40 % H_2O ones.

Moreover, comparison between the results obtained under conventional air combustion and different oxy-combustion environments can be also seen in Figure 4. The burnout under the 21/79 % O_2/CO_2 atmosphere is lower than that achieved under the 21/79 % O_2/N_2, what is an expectable result due the decrease of the gas temperature and the lower diffusivity of O_2 in CO_2 than in N_2 [31, 32]. The burnout degree under 21/39/40 % $O_2/CO_2/H_2O$ is even lower for this specific coal, but higher than the observed for the 21/54/25 % $O_2/CO_2/H_2O$ atmosphere. Anyway, the rising of O_2 concentration in oxy-fired conditions can compensate that issue; the burnout degree for the 30/30/40 % $O_2/CO_2/H_2O$ test significantly overpasses the value observed under air combustion.

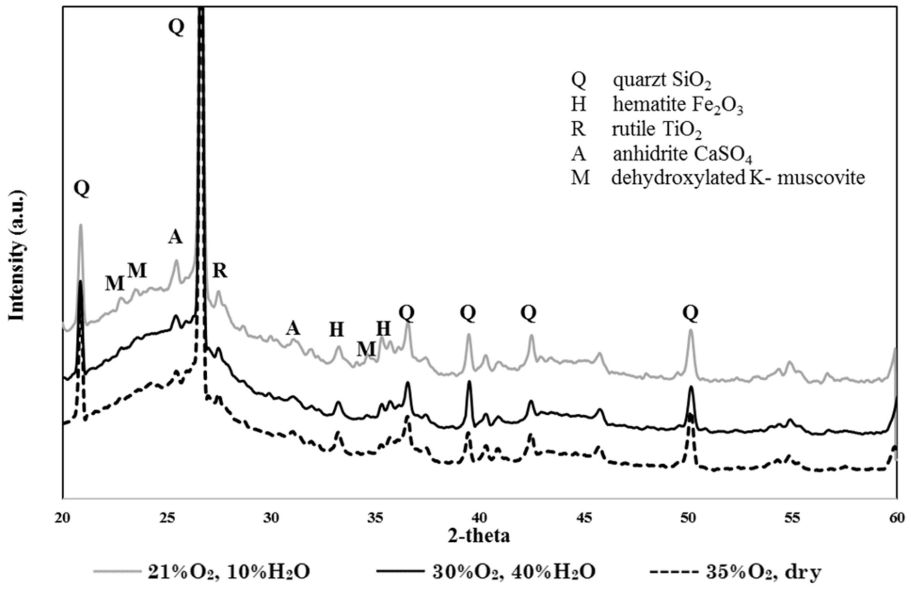


Figure 6.- Diffractograms of ashes from dry and wet oxy-combustion tests.

Aside from determining the burnout degree, collected solid residues were also used for XRD characterization. Figure 6 shows the diffractograms of ashes obtained for a selection of tests (35/65 % O_2/CO_2, 30/30/40 % $O_2/CO_2/H_2O$, 21/69/10 % $O_2/CO_2/H_2O$). All the solids presented the same characteristic quartz (SiO_2)

phase of high intensity, and a small presence of hematite (Fe_2O_3), rutile (TiO_2) and anhydrite ($CaSO_4$). Residues from the tests with lower burnout rates (21 % O_2), showed a small presence of dehydroxylated potassium muscovite. This indicates that aluminosilicates in initial mineral matter have been completely transformed into final quartz-like phase at 30–35 % O_2, which confirms that particles have reached higher conversion temperatures. It is worth mentioning that no differences were found when comparing ashes from dry and wet tests, which is an indication that H_2O addition has not effect in mineral matter evolution even under very high steam rates.

3.3 NO_x emissions

The effect of CO_2 replacement by H_2O on the NO emissions has been also characterized in $O_2/CO_2/H_2O$ atmospheres, for the same three oxygen concentrations (21, 30 and 35 %), varying steam fraction in the range 0–40 % for a fixed oxygen excess λ = 1.25. All the results shown in this section have been obtained from steady-state, mean NO concentration values. Maximum standard deviations of the recorded NO measurements during the tests were comprised in the range 0.97–3.84 % of the mean values. Fuel-N to NO mass conversion rates are gathered in Figure 7.

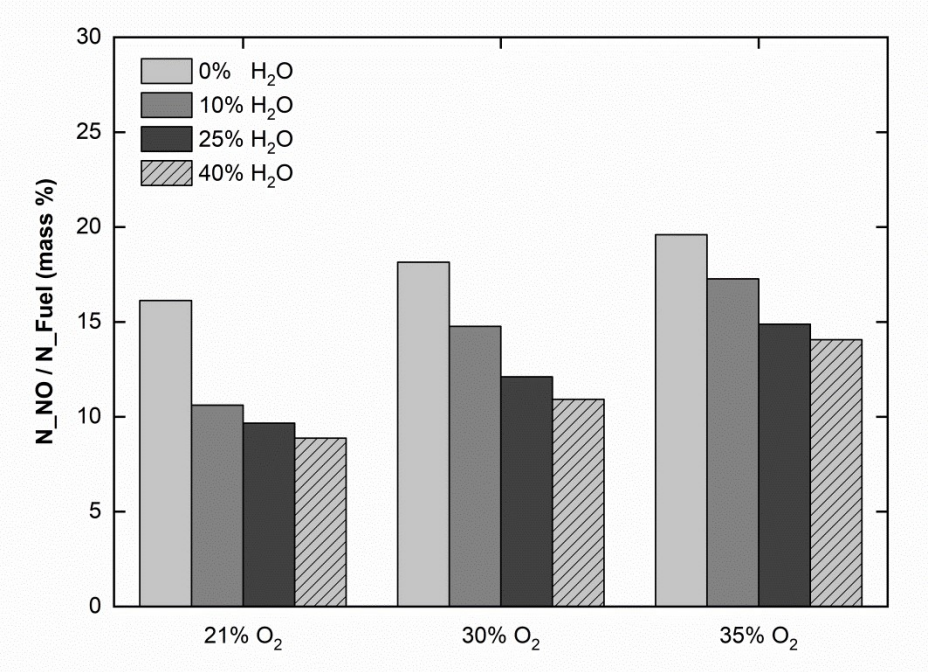


Figure 7.- Comparison of fuel-N to NO conversions obtained under different H_2O and O_2 conditions.

For all the conditions tested, the addition of steam reduces the NO formation. The larger the steam concentration, the larger the reduction rate obtained in comparison to the dry situation. Nevertheless, the reduction is not proportional to the steam content for the richest O_2 atmospheres, as also shown in Figure 8. Maximum reduction rates are obtained for the 40 % H_2O cases, ranging from around 45% for the 21% O_2 case to around 28% for the 35 % O_2 case.

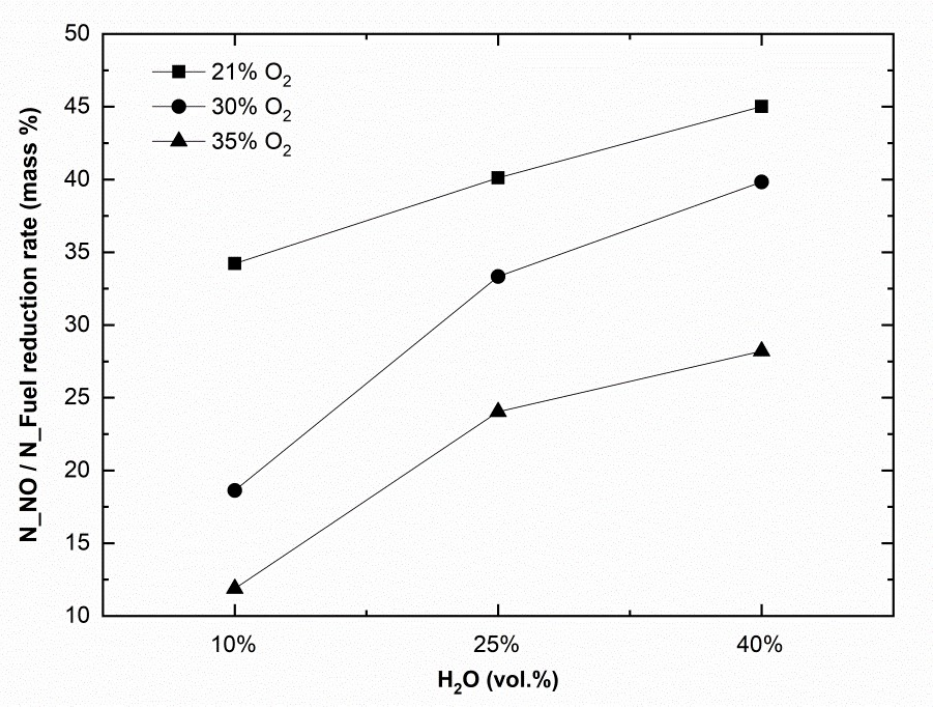


Figure 8.- Reduction rate of fuel-N to NO in comparison to the dry atmospheres, as a function of the steam concentration.

The results shown in Figures 7 and 8 are consistent with the mechanisms available in literature. Steam participates in the NO_x reduction of both the volatiles-N and the char-N. As concerns the volatile phase, HCN will be the main nitrogen-compound released in the case of high rank coals [33]. For temperatures over 800 ºC, the hydrogenation of HCN by steam contributes to reduce the NO formation [22]:

$$HCN + H_2O \rightarrow NH_3 + CO \quad (R1)$$

$$NH_3 + NO + 1/4\ O_2 \rightarrow N_2 + 3/2\ H_2O \quad (R2)$$

Moreover, the addition of steam promotes the presence of an OH/H radical pool that is involved in the NO_x chemistry [23] by competing with HCN oxidation:

382 $$H_2O \rightarrow H + OH \quad (R3)$$

383 $$HCN + H \rightarrow H_2 + CN \quad (R4)$$

384 $$HCN + OH \rightarrow H_2O + CN \quad (R5)$$

385 For high rank coals, the contribution of char-N to final NO_x is relevant, as
386 reported by Arenillas et al. [34]. Again, the radical H plays a role competing with
387 char-N oxidation:

388 $$C(N)_{char} + H \rightarrow HCN \quad (R6)$$

389 where the fate of HCN follows the mechanisms previously presented. Steam also
390 enhances char gasification, releasing CO. This carbon monoxide in the proximity of
391 the reacting particle can reduce NO by the reaction (R7), and also promotes the
392 increase of free carbon sites C^* in the char surface contributing to additional NO
393 reduction (R8) as reported in [35]:

394 $$CO + NO \rightarrow \tfrac{1}{2}\, N_2 + CO_2 \quad (R7)$$

395 $$C^*_{char} + NO \rightarrow \tfrac{1}{2}\, N_2 + CO \quad (R8)$$

396 Due to the very low amount of volatile matter in the fired coal, both
397 homogeneous reduction (R7) –catalysed on the char surface– and heterogeneous
398 reduction (R8) are playing a governing role in the results shown in Figure 7 and
399 Figure 8. The effect of steam on the gas-phase NO reduction is much more limited;
400 in fact, the replacement of CO_2 by H_2O can also contribute to an enhancement of
401 HCN and NH_3 oxidation due to the increase of oxidant diffusivity and flame
402 temperature.

403 Few studies are available in order to compare our results for high steam
404 concentrations (over 20%). To our knowledge, only Zhijun Sun et al. [23] have
405 reported results for steam addition up to 40 %. They showed that steam
406 contributed to diminish the NO formation, but with a concentration that minimized
407 the reduction rate. We have not detected this fact in our experiments, but the NO
408 reduction is clearly attenuated as steam addition grows. This could point out that
409 the optimum would be over 40% in our case.

410 Finally, Figure 9 displays fuel-N to NO mass conversion rates produced during
411 dry tests, for different oxygen excesses under air and three O_2/CO_2 atmospheres.
412 Besides showing trends depending on both the oxygen concentrations and excesses,

all consistent with other works [36–38], Figure 9 is interesting in order to independently compare the effect of oxygen excess with the effect of steam shown before in Figure 7. For all the tested atmospheres, a 40 % replacement of CO_2 by H_2O leads to a major impact on NO formation than the variation of oxygen excess in the range 1.25–1.45. Although O_2/CO_2 combustion prevents thermal-NO_x formation in comparison to air combustion, the increase of oxidant rates enhances fuel-NO_x formation. According to the results shown in Figure 7 and Figure 9, steam contributes to compensate that effect, enabling the rise of oxygen supply whereas lowering NO_x formation rates.

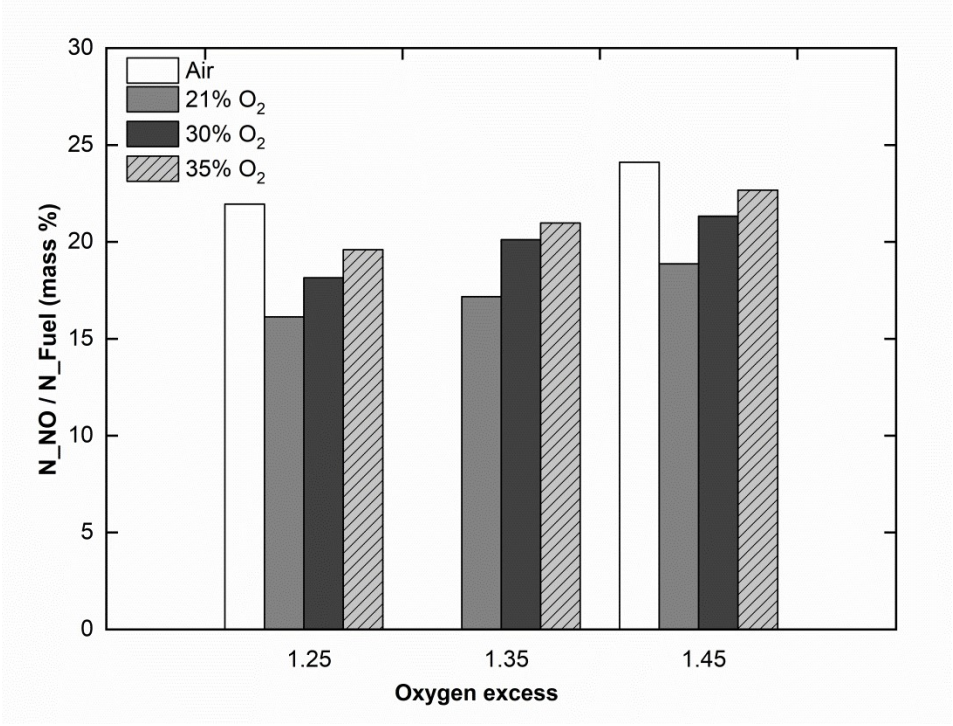


Figure 9.- Comparison of fuel-N to NO conversions obtained under different atmospheres and oxygen excesses, without steam addition.

Conclusions

An experimental lab-scale campaign has been completed aiming at determining the effect of large steam addition on the oxy-combustion characteristics of anthracite. The focus has been put on the ignition temperature, the burnout degree and the NO formation. Oxy-combustion tests have been conducted for three oxygen concentrations (21 %, 30 %, 35 %) while steam has been progressively added to the atmosphere in the range 10–40 %, replacing CO_2 as moderating agent.

The main insights from the experiments, carried out in an entrained flow reactor, can be summarized as follows:

- Steam addition initially advances the ignition of the anthracite, but a delay is observed when the steam concentration is further increased. Replacement of 40% CO_2 by H_2O leads to a very small variation of the ignition temperature.
- Steam concentration has a slight effect on the burnout degree, but much lower than the effect of the oxygen concentration. Variations in burnout degree due to 40% steam addition can be considered negligible for the richest O_2 atmospheres, while a decrease is observed for the 21% O_2 atmosphere in comparison to the dry case. This is explained by the very low volatile content of the fired coal.
- An outstanding decrease of NO formation is achieved by adding 40% steam, with a reduction ranging from about 28% to about 45% depending on the atmosphere. The NO decrease rate due to steam is attenuated as the atmosphere is enriched in oxygen content. The effect of steam has been proved to be more influential than the oxygen excess over stoichiometry.

Summing up, addition of up to 40 % steam in oxy-combustion hardly affects the ignition and conversion characteristics of the anthracite, while a relevant reduction of NO is achieved. The best combination is obtained for the 35/25/40 % $O_2/CO_2/H_2O$ atmosphere, joining high conversion and low emission rates: ignition temperature of 705 ºC, burnout degree over 78.5 % and fuel-N to NO conversion rate of 13.5%. Alteration of the solid residues composition is not observed after XRD analysis. These results supports that a transition from O_2/CO_2 combustion to O_2/H_2O combustion is feasible, at least as concerns the coal behaviour.

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